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STRUCTURAL, OPTICAL AND TOPOGRAPHICAL PROPERTIES OF SPRAY DEPOSITED CEO2 THIN FILM FOR VAPOUR SENSOR APPLICATION

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ABSTRACT

Thin film science has received tremendous attention in recent years because of numerous applications. CeO2 thin films with 0.1 molar concentration is prepared on glass substrate at 230°C using hepta hydrate cerium chloride (CeCl3.7H2O) solution. The aim of the present work is to investigate the structural, topographical, optical and sensing properties by XRD, AFM, UV and Chemiresistive gas sensing methods. XRD analysis revealed that the film is well crystallized in nature having cubic fluorite structure with a grain orientation along (220) plane. An average transmittance of 60% was observed in the visible region. AFM study shows that the particles are in agglomerate. The highest sensitivity 35% of the CeO2 gas sensor occur at 30 ppm concentration of NH3.

INTRODUCTION

Gas sensors are chemical sensors that are of paramount importance. As the air surrounding us contains different amount of gases which can be hazardous to human health, atmospheric pollutants are of significance to an industrial or medical process. It becomes therefore very imperative to detect the presence of these gases[1]. Due to the better

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electrical and optical properties of the thin film using rare earth metals, they are more suitable for the applications such as opto-electronic materials and fuel cells. Among various materials, CeO_2 is a popular material because of its standard properties for numerous biological and engineering applications. It has a wide band gap of 3.2 eV which also exhibits the oxidation states of both Ce^{+3} and Ce^{+4}. The transmission is very good in the visible and infra-red regions. It is an n-type semiconductor used most commonly because of its ease of preparation and flexibility in using the material. Cerium is the most abundant rare earth element, making up about 0.0046% of the earth's crust by weight (64 ppm), even more abundant than copper (60 ppm). It is found in a number of minerals, the most important being monazite and bastnasite. Cerium has four valence electrons $4f^26s^2$. It has two common oxidation states Ce(III) and Ce(IV). Cerium has 30 isotopes with atomic weights ranging from 123 to 152 g/mol. There are three stable isotopes: ^{136}Ce, ^{138}Ce and ^{140}Ce. The most abundant isotope is 140 Ce at 88.5%. Cerium resembles iron in color and luster, but it is soft, malleable and ductile. Cerium has the second-longest liquid range of any element: 2648 °C (795 °C to 3443 °C). It oxidizes easily in air and burns readily at 150°C to form cerium (IV) oxide. CeO_2 thin films can be deposited using various techniques such as pulsed laser deposition, sputtering, spray pyrolysis and spin coating. Among several methods, spray pyrolysis was used because of its low cost, capability to produce films in large area with uniform thickness, better doping with desirable ratios.

In the present work, CeO_2 thin films were prepared on glass substrates using the spray pyrolysis method. Investigation of the structural, topographical and optical properties using X-ray powder diffraction (XRD), AFM , UV-visible absorption spectrum indicate that the prepared product is well crystalline cubic phase of optically active nanoparticles are formed.

MATERIALS AND METHODS

Environmental pollution has received considerable attention due to their harmful effect on human health and living organisms[2-5]. The industrial progress causes several severe environmental problems by releasing wide range of toxic compounds to the environment[6][7]. Scrutinizing and investigation of these toxic materials in the environment is important from pollution controlling point of view. Ammonia (NH_3) is one of the most commonly produced industrial chemicals in the world.

The CeO_2 thin films are prepared by the spray pyrolysis process from a solution containing hepta hydrate cerium chloride ($CeCl_3.7H_2O$) in distilled water. The $CeCl_3.7H_2O$ solution is sprayed with a solution spray rate of 2ml/min onto a preheated glass substrate maintained at 230°C temperature, using compressed air as a carrier gas. Before spraying, the glass substrates are properly cleaned and annealed at 100°C for 30 min, in order to eliminate water molecules. The nozzle to substrate distance is about 20cm. The CeO_2 thin films thus obtained are transparent and exhibit good adherence to the substrate surfaces. X-ray diffraction (XRD) pattern was recorded with a "Xpert PRO" X-ray diffractometer using Cukα radiation. The optical transmittance and absorption characteristics were determined with a LAMDA 25 PERKIN ELMER spectrophotometer in the wavelength range of 300 – 1100 nm. The NH_3 gas sensing set up connected to a computer controlled National Instruments-Data acquisition data board (NI-DAQ 6212) Interface with Lab VIEW

software to record voltage is used. The electrical resistance of the film is thus obtained from voltage measurements.

RESULTS AND DISCUSSION

3.1 Structural Properties:

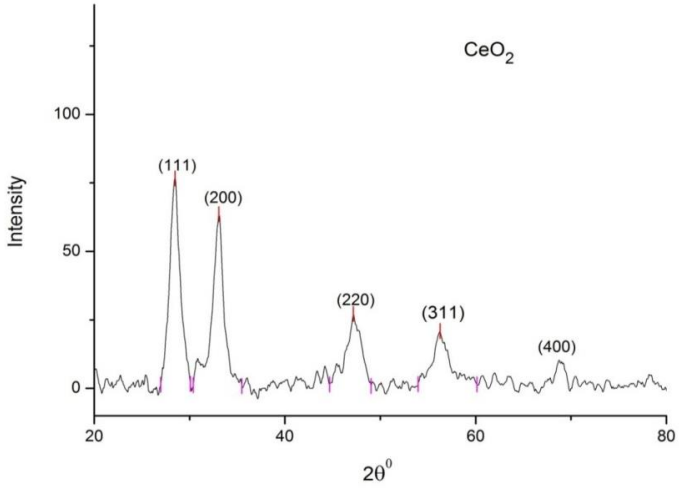
Figure 1 shows the XRD pattern of CeO_2 film with molarity (0.1 M) concentration prepared at 230°C on glass substrate. The strong and sharp peaks indicate good crystallization of the sample. XRD result indicates the formation of single phase CeO_2 with a cubic fluorite structure [JCPDS data (34-0394)]. No additional peaks were observed, revealing the high purity of the prepared CeO_2 thin film.

Grain sizes are calculated from XRD data using Scherer's formula as given below[8].

$$\text{Average grain size (D)} = \frac{0.9\lambda}{\beta \cos\theta} \qquad \textbf{(1)}$$

where D is the Crystallite size perpendicular to the normal line of (hkl) plane, ß is the full width at half maximum of the (hkl) diffraction peak, θ is the Bragg angle and λ is the wavelength of incident X-ray.

Fig. 1: *XRD Pattern of CeO2 Thin Films Prepared at 230°C*



To describe the preferred orientation, the texture coefficient TC (h k l), was calculated using the following expression.[8]

$$TC_{(hkl)} = \left[\frac{I_{(hkl)}}{\frac{1}{N}\sum \frac{I_{(hkl)}}{I_{o(hkl)}}} \right] \longrightarrow (2)$$

where $I_{(hkl)}$ is the measured relative intensity of a plane (hkl), $I_{0(hkl)}$ is the standard intensity of a plane (hkl) taken from the JCPDS data and n is the number of diffraction peaks considered in the calculation. It is clear from the definition that the deviation of texture coefficient from unity implies the film growth in preferred orientation. Texture coefficients calculated for (111) (200) (220) (311) and (400) planes are shown in the table 1. The higher value of TC indicates the preferred orientation of the films along that diffraction

plane. This means that the increase in preferred orientation is associated with the increased number of grains along that plane. The high value of TC along (220) plane indicates the maximum preferred orientation of the films along the (220) diffraction plane.

Table 1: *Texture Coefficient Calculated for CeO_2 Thin Film for Various Peaks*

Peaks (hkl)	111	200	220	311	400
TC	0.983027	0.35129	1.533522	1.446478264	0.685685119

The lattice parameter can be calculated from the prominent peaks using the equation [9]

$$a = \frac{\lambda}{sin\theta}\sqrt{h^2 + k^2 + l^2} \longrightarrow \quad (3)$$

The calculated particle sizes and lattice parameter of the as-prepared ceria films from XRD spectra are shown in table 2. The grain size is found to change with diffraction plane.

Table 2. *The grain size, lattice parameter and dislocation density calculated with respect to different peak values*

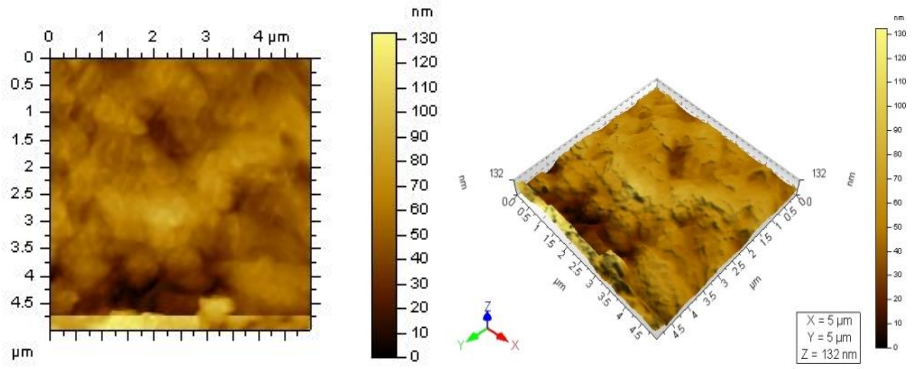
Peaks (hkl)	111	200	220	311	400
Grain Size (nm)	10	12	7	7	9
Lattice parameter	3.454183	3.320633	4.38834	6.143011	9.784917
Dislocation Density(x10^{14}lines/m^2)	0.84168	0.685277	0.02	0.02	0.013956

From table 2, an increase in the lattice parameter and dislocation density was observed with a decrease in crystallite size. As a general rule, nanoparticles of oxides exhibit a lattice expansion with reduction in particle size while metal nanoparticles exhibit a lattice contraction[10]. This lattice expansion with concentration is attributed to the lattice strain induced by the increase of Ce^{3+} ions due to the formation of oxygen vacancies [11].

3.2. Topographical Property

Figure 2 shows the AFM analysis of CeO_2 thin films prepared at 230°C. It indicates that the film prepared with concentration of 0.1 molarity shows agglomerate particles with pores. The formation of some cracks observed in the thin film may be due to the thermal stress during the deposition. The surface of the film is very dense and packed closely with each other.

Fig. 2: *AFM 3D Images of CeO_2 at 230° C*



3.3. Optical Properties

The figures 3 (a) and (b) show the transmission and absorption spectra of CeO_2 film of (0.1 M). These measurements were recorded in the wavelength range of 200 – 1100 nm at room temperature using glass substrate. The prepared film attains better transparency in the visible region, which indicates that the film is uniform and also well adhered to the glass substrate. An average transmittance of 60% is reached for the film. The Fig 3a shows a broad absorption band located at 334 nm in the UV range; one could suggest that the higher concentration of grain boundaries is responsible for broadening the absorption edge[12][13]. The wave length of maximum absorption 336 nm (fig. 3a) depends on the presence of particular chromophores in a molecule. The transmittance of cerium oxide (CeO_2) thin film shown in fig.3 (b) indicates that the transmittance in the UV region decreases to zero and increases with wave length (λ) in the visible region. The high transmittance (above 60%) in the visible region is probably due to the existence of an interfacial layer with low refractive index between CeO_2 and glass plate[13]. It could be observed that the band gap energy is of 3.69 eV calculated from the below formula[14].

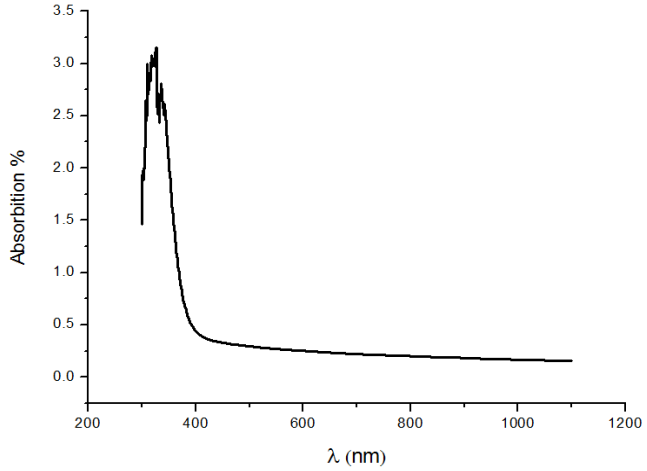


Fig. 3 (a) Absorbance Spectra of CeO_2 thin film

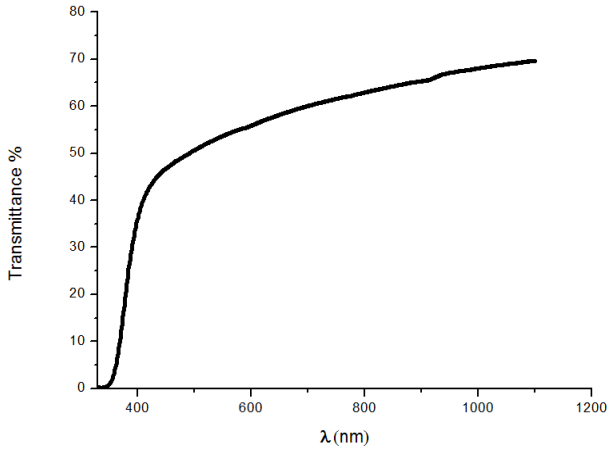


Fig.3 (b) Transmittance Spectra of CeO_2 thin film

$$E_{bg} = \frac{1200}{\lambda} \text{ (eV)} \longrightarrow (4)$$

where E_{bg} is the band-gap energy and λ is the wavelength (nm). The value of band gap energy agrees well with values reported by 4.16 eV et al[14]

3.4. GAS SENSING PROPERTIES

The sensing response of the thin film was investigated against the temperature; the response of the film starts at a lower temperature at 33ºC and is almost linearly increasing with temperature up to 224ºC and has a steady response then on up to 324ºC after which a decline was noted (Fig 4). From the temperature dependence of the sensing behaviour, it can be suggested that the film can be operated best in the temperature region of 224ºC to 324ºC.

Fig. 4: *Sensing Response vs. Operating Temperature*

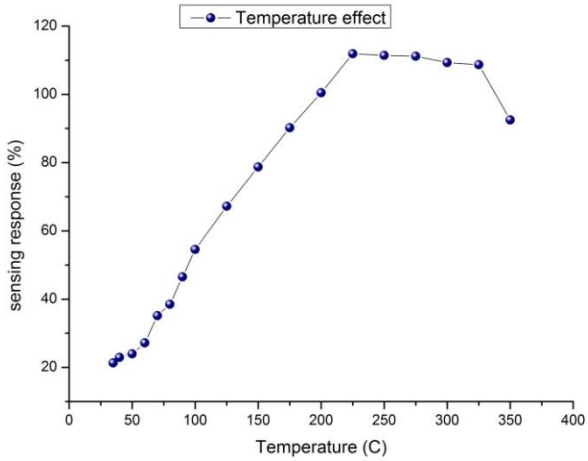


Table 3: *Response, Recovery and Sensitivity Values of CeO_2 Thin Film with Different Concentration of NH_3*

Ammonia Vapour Concentration (PPM)	Response time (Sec)	Recovery time (Sec)	Sensitivity (%)
05	18	26	16
30	17	33	30
40	50	29	17
50	22	73	19
60	34	66	19
70	36	55	19

The response of the relative target gas was calculated by the ratio of change in resistance of a sample upon exposure and original gas resistance in air. The response formula can be written as[15]

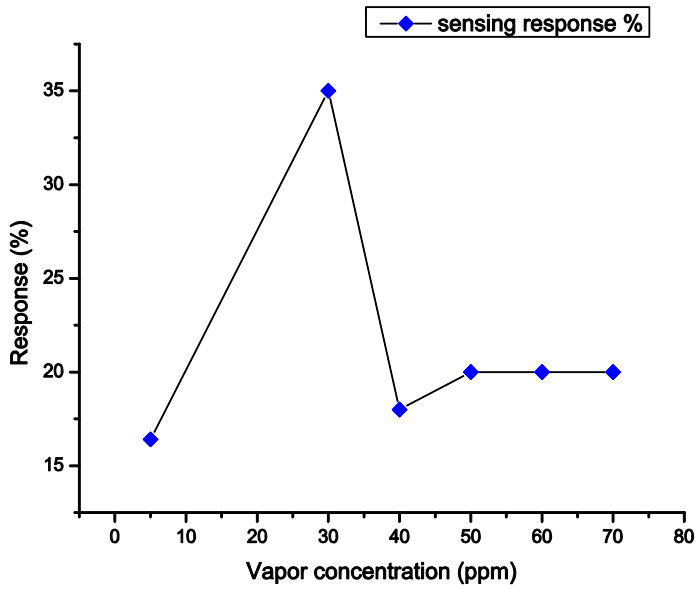
$$\text{Target gas response (TGR)} = \frac{R_a - R_g}{R_a} \text{ X } 100 \longrightarrow \quad \textbf{(5)}$$

R_a=Resistance in air, R_g = Resistance in target gas

Response time (RPT) was construe the time required for a sensor to obtain 90% of the ultimate value in resistance after exposure of the sensor surface to a target gas, while recovery time taken to get back 90% of maximum resistance[16] in air. This material showed significantly higher responses and recovery time when exposed to the target gas and then air, respectively. Table 3 shows the response and recovery times of the sensor at various concentration of target gas.

The sensitivity of the material is calculated from the TGR formula and the values are shown in the fig.5. The highest sensitivity (35%) of the CeO_2 gas sensor occurs at 30 ppm concentration of NH_3. Therefore CeO_2 can be a beneficial material for the fabrication of NH_3 gas sensors. The results show great promise for cheaper air quality measurement, the use of the operating temperature around 224ºC to 324ºC helps to lower power requirement.

Fig.5. *Sensitivity of Pure CeO_2 Thin Film Operating at Different Vapor Concentrations*



CONCLUSION

The spray pyrolysis technique was employed to deposit CeO_2 thin films of 0.1M at 230°C. The structural, topographical and optical analysis of the deposited film was investigated. XRD analysis reveal that the film is well crystallized in nature having cubic fluorite structure with a grain orientation along (220) plane. UV-Visible spectra show that the films are transparent (60%) in the visible region with the band gap of 3.69 eV. Due to its nano-crystalline nature, the deposited CeO_2 thin films are investigated for gas sensing application. It was found that CeO_2 thin film has high sensitivity at low (35 ppm) concentration of NH_3 and good sensing behaviour with short response and recovery time at low temperatures (224ºC to 324ºC). This sensing property may find use in monitoring environment.

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